Engineering supramolecular architectures on insulating and metal surfaces studied by scanning tunneling microscopy

Sun, Xiao

Summary

The development of organic devices with nanoscale features is becoming the focus of intense research activity. Organic electronics has the potential to revolutionize the fabrication of computers and other electronic devices. “Electronic newspapers”, smart windows, flexible film solar cell sheets, luminescent wallpaper are only a few examples of future electronic devices based on organic electronics. Thin films of organic molecules and polymers are expected to be used as active layers to replace the inorganic materials such as silicon. Engineering efficient organic devices requires selecting organic materials with optimal electronic properties and building optimized organic structures. Therefore the fabrication of the next generation of organic devices begins with understanding and control of assembly at the molecular scale to produce new devices having advanced properties.

Investigation of supramolecular assembly on various surfaces is motivated by the potential of future organic electronics. Since the publication of the first “plastic transistor” (poly-thiophene) by Tsumura et al. in 1987, there has been considerable interest in the development of organic solar cells and organic transistors. The organic devices are usually composed of an active organic layer deposited on a metal or an insulating surface. Organic device performances are limited by structural defects in the organic layer and defects at the organic / substrate interface. It is therefore required to control the formation of defect free molecular structures and to characterize the interaction of the molecules with the substrate surface. Self-assembly processes are one of the most promising methods to engineer complex molecular architectures on various substrates. Adsorption, mobility, and intra- or intermolecular interactions, all of which depend on the substrate crystalline lattice, chemical nature, and symmetry are key parameters that govern the formation of molecular architectures. A balance between molecule-molecule and molecule-surface interactions is at the origin of the formation of supramolecular order.

Insulating thin films have been investigated in recent years. They are “ideal” candidates for technological applications. Insulating thin films can form flat and defect free crystalline layers on metal surfaces. In addition, when building a device it is advantageous if the insulating thin film are easy to prepare and their thickness easy to control.

In the second chapter of this thesis, I briefly described the experimental technique I used in this research project. The scanning tunneling microscope, the UHV system, the deposition of molecular layers and the Au(111)-(22×√3) superstructure are discussed.

Scanning Tunneling Microscopy is a powerful technique which provides the possibility to achieve atomic scale images of the electronic density of states in real space. The rapid development of the technique over the past 20 years enables a resolution good enough to image atoms from the material and organization of molecules on the surfaces. The STM in vacuum is used for the surface characterization.

The STM technique is based on the quantum mechanical tunneling effect. According to the theory, when a conductive tip is approaching to the sample and a bias voltage is applied between the tip and the sample, electrons will tunnel though the vacuum barrier between the two. The resulting current is called the tunneling current which is proportional to the local density of states (LDOS) of the sample (where the local density of states of the tip is considered as constant). From the detected current, high resolution topography of the sample is deduced.

Ultra high vacuum is necessary to prepare clean samples and to image the surfaces with high resolution in a clean environment. Au(111)-(22×√3) on mica cleaned in vacuum was chosen as substrates for all the experiments. The high resolution Au(111)-(22×√3) superstructures observed indicated a perfectly clean crystalline gold substrate. The NaCl and other organic molecules were deposited in vacuum by thermal sublimation.

In the third chapter of my thesis, I report on my investigation of the formation of multi-component self-assembled supramolecular architectures on metal surfaces. I first mixed PTCDA and melamine molecules on an Au(111)-(22×√3) surface. The perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) molecule is an archetypal organic semiconductor which is a potential building block for the realization of organic electronic devices. Assessing and tailoring PTCDA assemblies are of technological interest for optimizing the design of organic thin film electronic devices. PTCDA is a versatile molecular building block for its ability to form hydrogen bonds with other molecular species. Mixing differently shaped molecules is expected to lead to the formation of sophisticated supramolecular structures. PTCDA has a rectangular shape whereas 1,3,5- triazine-2,4,6-triamine (melamine) has a triangular shape. PTCDA and melamine can form O···H-N hydrogen bonds on Au(111). The resulting 2D PTCDA-melamine assemblies deviate from pure PTCDA and pure melamine network structures.

I investigated the formation of three PTCDA-melamine supramolecular networks on Au(111)- (22 × √3). Different chiral supramolecular networks were formed by tuning the ratio of the molecules deposited on the surface at room temperature. Scanning tunneling microscopy (STM) revealed that supramolecular networks having a PTCDA: melamine ratio of 3:2, 1:2, 1:4 can be selectively created. The 3:2 and 1:4 PTCDA-melamine networks have never been reported before. From experimental STM images of supramolecular structures I determined the various molecular bonding schemes driving the different molecular self-assemblies. I identified 10 different PTCDA-melamine building blocks. These results reveal that molecular ratio is a key parameter driving multi-component supramolecular architectures. I also investigated the influence of the temperature on PTCDA-melamine self-assembly. PTCDA and melamine molecules form a 3:2 chiral supramolecular network at room temperature and annealing at 80°C switches the ordering into a completely different 1:2 row-like supramolecular network. This temperature-induced switching is not reversible.

Among the three PTCDA-melamine supramolecular networks, the PTCDA: melamine 3:2 network is an open structure. It can be used as a nano-template for hosting guest molecules. C_{60} was tried as guest molecules, however, the size of C_{60} molecule is too large to be trapped into the 3:2 PTCDA-melamine network cavities. The PTCDA-melamine network acts as an organic layer which decouples the C_{60} hexagonal network from the Au surface.

I also investigated the self-assembly of PTCDA-Adenine architecture on Au(111). A very complex supramolecular network was observed using STM. This network with a large unit cell which includes 14 molecules is chiral and has a molecular ratio of 5:2 (PTCDA: adenine).

To control and fabricate organic layers on insulating thin films is important to develop organic devices such as OFET. In the fourth chapter of my manuscript, I describe my study of the formation of PTCDA (3,4,9,10-perylene-tetracarboxylic-dianhydride) nanostrutures on Au(111) covered with NaCl islands. I first grew NaCl layers on Au. STM images show that these layers are crystalline NaCl(100) films. NaCl(100) islands preferentially nucleate along the Au(111) step edges. Atomic resolution was achieved and the atomic images of different domains indicates a epitaxial growth of NaCl(100) on Au(111). My STM measurements reveal that different NaCl(100) layers can selectively be imaged by changing the tunneling parameters, and that the NaCl layer heigh is depending of the tunneling parameters.

I then deposited PTCDA molecules on an Au surface covered with NaCl(100). I observed that PTCDA molecules preferred to form 2D domains on bare Au(111) surface at the edge of NaCl(100) islands on a partially covered gold. Conversely, PTCDA formed 3D

clusters along the step edges of the NaCl(100) domains when the gold surface was fully covered by the NaCl(100) islands. The growth of epitaxial PTCDA 2D domains on NaCl(100) appeared to be energetically unfavorable. PTCDA molecules preferred assembly in 3D clusters rather than forming 2D layers on the NaCl(100) thin film surface. This contrasts with previous observation, where it was observed that PTCDA grows as layers or differently shaped nanocrystals on the (100) surface of a NaCl single crystal. This highlights that the experimental conditions and the NaCl(100) surface preparation are key parameters driving the PTCDA growth on NaCl. Our results suggest that the properties of NaCl(100) thin film surface grown on Au(111)-(22×√3) differ from those of the single crystal NaCl(100) surface. In contrast with NaCl(100) single crystal surface, 2D ordered PTCDA monolayers do not form on the NaCl(100) thin film on Au(111)-(22×√3) Further deposition of PTCDA molecules therefore does not lead to the formation of PTCDA multilayer islands or PTCDA nanocrystals but leads to the formation of PTCDA 3D clusters.

In conclusion, I succeeded in forming PTCDA-melamine and PTCDA-adenine supramolecular architectures on Au(111). In the case of PTCDA-melamine networks, I showed that molecular ratio and temperature permit to tune molecular ordering. This is not the case with PTCDA-adenine structures. In addition, I used STM to characterize NaCl(100) layers on Au(111). I showed that the NaCl aspect is depending on the tunneling parameters. Using STM, I also investigated the self-assembly of PTCDA molecules on NaCl/Au(111)-(22×√3). At sub-monolayer NaCl coverage, PTCDA molecules form molecular 2D domains on the Au(111) surface. NaCl(100) island step edges act as preferential nucleation sites. At high NaCl coverage, PTCDA molecules form 3D clusters decorating the step edges of NaCl(100) islands.